BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C10L 1/22

A1

(11) International Publication Number: WO 96/21709

(43) International Publication Date: 18 July 1996 (18.07.96)

(21) International Application Number: PCT/EP96/00084

(22) International Filing Date: 9 January 1996 (09.01.96)

(30) Priority Data:
9500460.2 10 January 1995 (10.01.95) GB

(71) Applicant *(for all designated States except US)*: EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CAPROTTI, Rinaldo [IT/GB]; 5 Cumnor Rise Road, Oxford, Oxfordshire OX2 9HD (GB). COLE, Roy, D. [GB/GB]; 1 Orchard Gardens, West Challow, Wantage, Oxfordshire OX12 9TL (GB).

(74) Agents: NORTHOVER, Robert, Frank et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).

(81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: FUEL COMPOSITIONS

(57) Abstract

A fuel oil composition comprising a major proportion of a liquid hydrocarbon middle distillate fuel oil having a sulphur content of not greater than 0.2 % by weight of the fuel oil and a minor proportion of a hydroxy amine which improves the lubricity of the fuel oil. The inclusion of the hydroxy amine in the fuel also markedly reduces the foaming tendency of the fuel oil.

FUEL COMPOSITIONS

This invention relates to the use of an additive for providing a low sulphur fuel oil with improved lubricity and other benefits and to fuel oil compositions containing the additives.

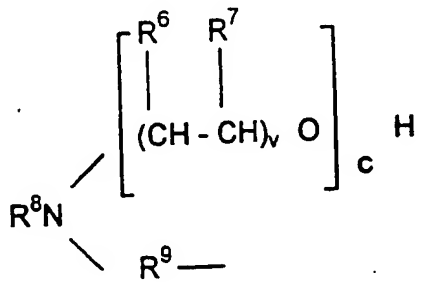
US-A-4,409,000 describes additives for normally liquid fuels for providing carburettor and engine detergency. A combination of at least one hydroxyl amine of specified formula and at least one hydrocarbon soluble carboxylic dispersant is proposed for inhibiting the formation of sludge in the carburettor and engine. The sole exemplification relates to the use of such combinations of ingredient in gasoline. Apart from the statement that the compositions provide carburettor and engine detergency no other information is provided as to properties provided by these compositions.

US-A-2,527,889 describes polyhydroxy alcohol esters as primary anti-corrosion additives in diesel engine fuel, and GB-A-1,505,302 describes ester combinations including, for example, glycerol monoesters and glycerol diesters as diesel fuel additives, for combinations being described as leading to advantages including less wear of the fuel-injection equipment, piston rings and cylinder liners.

GB-A-1,505,302 is, however, concerned with overcoming the operational disadvantages of corrosion and wear by acidic combustion products, residues in the combustion chamber and in the exhaust system. The document states that these disadvantages are due to incomplete combustion under certain operating conditions. Typical diesel fuels available at the date of the document contained, for example, from 0.5 to 1 % by weight of sulphur, as elemental sulphur, based on the weight of the fuel.

The sulphur content of diesel fuels has now been or will be lowered in a number of countries for environmental reasons, i.e. to reduce sulphur dioxide emissions. Thus, heating oil and diesel fuel sulphur content are being harmonised by the CEC at a maximum of 0.2% by weight, and, at a second stage, the maximum content in diesel fuel will be 0.05% by weight. Complete conversion to the 0.05% maximum may be required during 1996.

The process for preparing low sulphur cont nt fuels, in addition to reducing sulphur content, also reduces the content of other components of the fuel such as



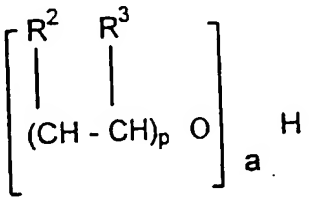
where each of R^2, R^3, R^4, R^5, R^6 and R^7 is independently hydrogen or a lower alkyl radical; R^8 is an alkenyl radical having one or more double bonds or an alkyl radical and containing from 4 to 50 carbon atoms; R^9 is an alkylene radical containing from 2 to 35, e.g. 2 to 6, carbon atoms; each of p, q and v is an integer between 1 and 4; and each of a, b and c may be 0, providing that at least one of a, b or c is an integer between 1 and 75.

A second aspect of the invention is the use of a fuel oil composition as defined in the first aspect of the invention as the fuel in a compression-ignition (diesel) engine for controlling wear rate in the injection system of the engine in operation of the engine.

A third aspect of the invention is a method of operating a compression-ignition (diesel) engine comprising providing a fuel oil composition as defined in the first aspect of the invention as the fuel in the engine thereby to control wear rate in the injection system of the engine.

The examples of this specification will demonstrate the efficacy of the hydroxy amine additives defined under the first aspect of the invention in reducing wear when fuel oils having a sulphur content of not greater than 0.2% by weight are used.

Whilst not wishing to be bound by any theory, it is believed that the additive, in use of the composition in a compression-ignition internal combustion engine, is capable of forming over the range of operating conditions of the engine, at least partial mono- or multi-molecular layers of the additive on surfaces of the injection system, particularly the injector pump that are in moving contact with one another, the composition being such as to give rise, when compared with a composition lacking the additive, to one or more of a reduction in wear, a reduction in friction, or an increase in electrical contact resistance in any test where two or more



when a is 1, or indirectly via an oxyalkylene or polyoxyalkylene linking group (when, for example, a is 2 or more. The hydroxy alkyl group and the oxyalkylene units of any linking group may contain from 2 to 6 carbon atoms, optionally substituted with lower alkyl radicals. By 'lower' alkyl is meant an alkyl group containing 6 or less carbon atoms. Preferably, p, q and v, if present, are equal to 1.

The hydroxy alkyl group and the oxyalkylene units of any linking group may together form a chain having up to 75 units including the terminal hydroxy alkyl group. Preferably the number of oxyalkylene units does not exceed 10. The most preferred number represented by a, b and c in the structural formula is 1 for each of a, b and when present, c.

The radicals R^2, R^3, R^4, R^5, R^6 and R^7 are preferably hydrogen or methyl.

In the structural formula, R^9, if present, is preferably an alkylene radical containing from 2 to 6 carbon atoms, which may be a straight or branched chain of carbon atoms.

Suitable hydroxy amines may be prepared by reaction of amine, substituted with an appropriate R^1 or R^8 group and having residual amine functionality, with an alkylene oxide, such as ethylene oxide or propylene oxide. Suitable ethoxyamines are commercially available from Armak Company under the trade names 'Ethomeen' and 'Ethanolomeen'.

The concentration of hydroxy amine which is effective in significantly improving the lubricity of the fuel is extremely low and may readily be determined by the wear tests identified in the Examples. In general, a noticeable reduction in wear is observed using as little as 5 ppm of additive by weight of fuel. Preferred concentrations range from 10 ppm to 0.2% by weight. Although higher concentrations may be used the wear test should be used to determine the

isoparaffins; and alkoxyalkanols. The carrier liquid must of course be selected having regard to its compatibility with the additive and with the fuel.

CO-ADDITIVES

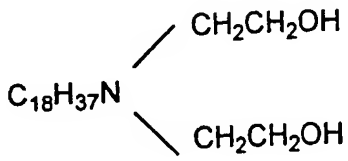
The additives of the invention may be used singly or as mixtures of more than one additive. They may also be used in combination with one or more co-additives such as known in the art, for example the following: detergents, antioxidants (to avoid fuel degradation), corrosion inhibitors, dehazers, demulsifiers, metal deactivators, antifoaming agents, cetane improvers, cosolvents, package compatibilisers, and middle distillate cold flow improvers.

EXAMPLES

The following examples illustrate the invention. The following materials and procedures were used and the results are tabulated below.

Additives

A. An hydroxy amine of formula



Fuels

I: a middle distillate fuel oil having the following characteristics-

- sulphur content (wt %) <0.01
- viscosity at 20°C (cSt) 2.486
- density at 15°C (Kg/dm^3) 0.8136

II: a standard kerosene fuel such as commercially available

Example 2

Additive A was added to fuel oil III at various concentrations and the antifoam performance was measured at 0°C. The test used was as follows:

Each sample was agitated vigorously for a period and the time, in seconds, for the foam to collapse was then observed. The results of the untreated and treated fuels are compared in the table below.

	Additive A Concentration (ppm, weight/weight)	Foam Collapse Time (sec) (Average of 2 readings)
Fuel III	0	83.5
	5	40
	50	35
	500	15.5

These results show a marked reduction in the tendency of the fuel to foam when Additive A is present.

3. A fuel oil composition according to claim 2 wherein the sulphur content is not greater than 0.01 % by weight.

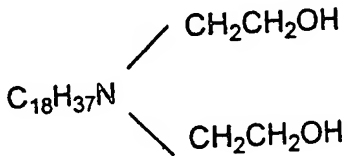
4. A fuel oil composition according to any one of the preceding claims wherein R^1 or R^8, if present, contains from 8 to 30 carbon atoms.

5. A fuel oil composition according to any one of the preceding claims wherein a, b and c, if present, do not exceed 10.

6. A fuel oil composition according to any one of the preceding claims in which R^2 to R^7 are either hydrogen or methyl.

7. A fuel oil composition according to any one of the preceding claims in which the concentration of hydroxy amine is from 1 ppm to 2000 ppm by weight of the fuel oil.

8. A fuel oil composition according to any of the preceding claims wherein the hydroxy amine is of the formula:



9. The use of a fuel oil composition as claimed in any one of the preceding claims as the fuel in a compression-ignition engine for controlling wear rate in the injection system of the engine in operation of the engine.

10. A method of operating a compression-ignition engine comprising providing a fuel oil composition according to any one of claims 1 to 8 as the fuel in the engine thereby to control wear rate in the injection system of the engine.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/00084

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 482 253 (ETHYL) 29 April 1992 see page 8, line 35 - line 36 see page 9, line 40 - line 47	1-10
Y	EP,A,0 348 236 (EXXON) 27 December 1989 see abstract see page 14, line 16 - line 17	1-10
A	EP,A,0 237 356 (EXXON) 16 September 1987 see page 11 - page 14	1-10
A	FR,A,1 361 104 (ARMOUR AND COMPANY) 28 August 1964 see the whole document	1-10
A	US,A,3 873 278 (POLSS) 25 March 1975 see the whole document	1-10
A	GB,A,2 260 337 (ETHYL) 14 April 1993 see page 3, line 15 - line 19 see abstract	1-10
A	US,A,3 235 501 (WALDMANN) 15 February 1966 see the whole document	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 96/00084

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3873278	25-03-75	CA-A-	1008664	19-04-77
		DE-A-	2456574	05-06-75
		FR-A,B	2253083	27-06-75
GB-A-2260337	14-04-93	CA-A-	2079049	12-04-93
US-A-3235501	15-02-66	NONE		